Novel Materials from Molecular Solids under Pressure

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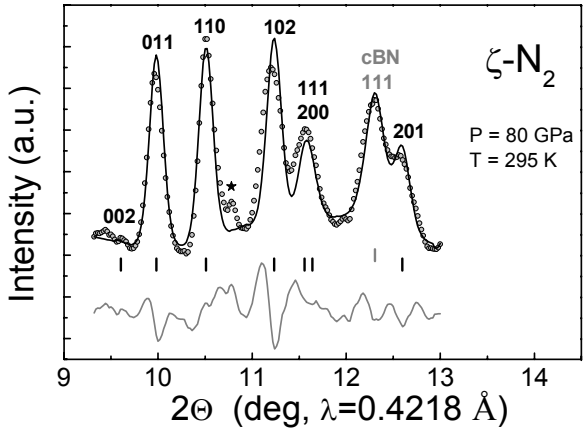
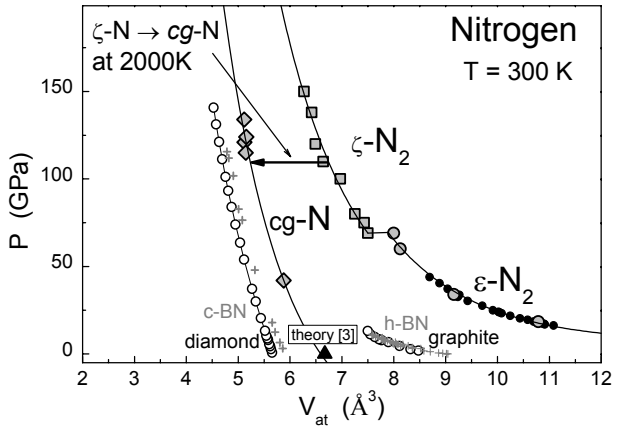
Transforming molecular nitrogen to a single-bonded atomic solid is of great fundamental interest; it also is among the most energetic non-nuclear materials yet predicted to exist.

X-ray diffraction to 170 GPa with diamond cells at the APS revealed a transition at 60 GPa from the rhombohedral (*R*3*c*) ε-N_2 to the (*P*222$_1$) ζ-N_2 phase.

Near 110 GPa (with heating) the single-bonded framework phase forms having the *cubic gauche* structure (*cg*-N) with a density increase of 22%.

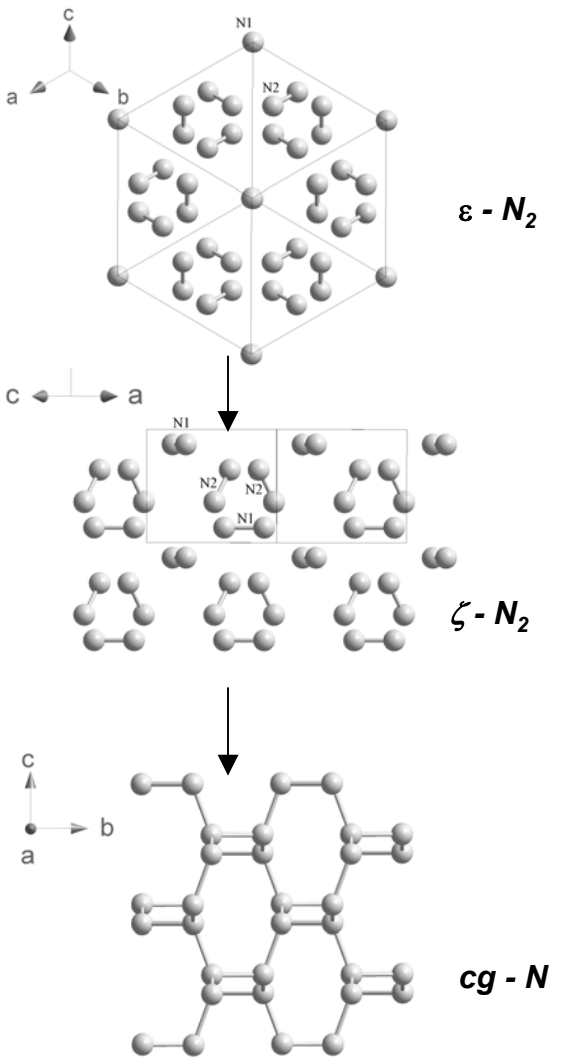


X-ray diffraction pattern of nitrogen. at 80 GPa refined for ζ -N_2 and cBN (gasket material).



P-V relations for the high-pressure phases of nitrogen determined from x-ray diffraction.

[Eremets et al., *Nature Materials* 3, 558 (2004); Eremets *et al., J. Chem. Phys.,* submitted]



Pressure-induced transformations culminating in the framework structure

The study of homonuclear diatomic molecular solids (e.g., H_2, O_2, N_2) under high pressure is one of the fundamental problems of condensed matter physics. At low pressures, atoms are strongly covalently bonded in the molecules that in turn weakly interact with each other. At high pressures, inter- and intra-molecular interactions become comparable, ultimately leading to dissociation of molecules. Experimental study of such transformations is a benchmark test for modern theories of the solid state.

Nitrogen exhibits characteristics of special interest as an archetypical molecular system. Diatomic molecular nitrogen has the greatest binding energy (after CO) and the shortest bond length, a unique elemental diatomic molecule with triple covalent bonds. First-principles theory has predicted that under high compression, molecules dissociate so that each of the nitrogen atoms has three single covalent bonds to form a three-dimensional covalent solid [1]. Calculations also predicted that the phase should crystallize in the cubic gauche (*cg*-N) structure where all nitrogen atoms are three-fold coordinated and the bond lengths are the same for all pairs of bonded atoms [2]. Due to its similarity to the diamond structure (with tetrahedral bonding), *cg*-N could be called as a “nitrogen diamond.”

Previously, we studied the high-pressure phases using spectroscopic and electrical conductivity techniques [3,4]. Here we used new high-pressure x-ray diffraction techniques at the Advanced Photon Source (HPCAT, Sector 16) to probe the pressure-induced transformations in this material. We determined the crystal structure, lattice parameters, compressibility, and transformation pressures. These properties for the both the high-pressure molecular phase and the non-molecular (framework or diatomic) phase were determined for the first time. The structures give insight into the transformation mechanisms. A very large energy is expected to be released at the transformation from polymerized nitrogen to diatomic molecular nitrogen. Thus, nitrogen may form a high energy density material with energy content higher than that of any known non-nuclear material.

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3. A. F. Goncharov, E. Gregoryanz, H. K. Mao, Z. Liu, and R. J. Hemley, Phys. Rev. Lett. **85** (6), 1262 (2000).
4. M. I. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz, Nature **411**, 170 (2001).